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Production of biodiesel using high free fatty acid feedstocks

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ABSTRACT

The enormous challenges faced in the search for suitable and profitable feedstocks to produce biodiesel cannot be over-emphasis. This paper has provided an overview of different catalysts used in processing different kinds of feedstocks for the production of biodiesel. Although the process of biodiesel production from refined feedstocks is less cumbersome and could provide biodiesel yield of more than 98%, but its product cost is high. Thus, the recent biodiesel production from low-quality feedstocks, though presents challenges but has equally provided biodiesel yield comparable to that obtained from refined feedstocks. Furthermore the physicochemical properties of biodiesel derived from low-quality feedstocks are discussed. Additionally economic evaluation of biodiesel from low-quality feedstocks is examined. The result showed that if less expensive feedstocks are used to produce biodiesel, a 25% reduction in cost production is possible. Thus making biodiesel price reasonably closed to the price of petro-diesel.

Contents

1. Introduction

Realization of suggestions of Madrid Declaration and provisions of Kyoto Protocol to reduce greenhouse gas emissions as CO_2, CO, SO_2, etc. requires introduction of new substitute fuels from renewable energy resources [1]. As well, requirement of high-energy in the developed countries, as much in the domestic sector, as in industry and transport, its raise in price, and the problems associated with use of non-renewable fossil fuels, etc., makes it even more essential to develop renewable sources of energy of unlimited period and lesser environmental effects than the conventional ones [2,3]. Additionally, in the last century the energy consumption globally has increased by 22.6-fold [4]. As a result the World energy demand in 2002 was 3.8×10^{18} GJ and nearly 81% of it was derived from fossil fuels [5]. Another report showed that fossil fuel account to 88% of the main energy consumption, with coal (29%), natural gas (24%) and oil (35% share) as the key fuels. And hydroelectricity and nuclear energy account for 6% and 5% respectively of the total primary energy consumption [6]. Therefore, the search for alternative biofuels such as biodiesel is increasingly becoming important Worldwide. Biodiesel as a

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renewable energy source has great potential to be used as a substitute fuel in diesel engines [7–11]. Besides, the environmental benefits associated in burning biodiesel fuels such as lower emissions of particulate matter and greenhouse gases for instance CO, SO_x and CO_2 [12–19]. Thus the reductions in net CO_2 emissions are projected in Philippines at 80.8–109.3% of diesel displaced by coconut biodiesel [20]. In the United States, the driving force behind the search for biodiesel fuels is primarily environmental concerns [21]. Recent study showed that use of biodiesel can decrease 95% of cancers and 90% of air toxicity and provide clean environment [22,23].

Biodiesel fuel derived from fats and oils offers several advantages compared to petro-diesel fuel. These advantages are, it provide lower hydrocarbon and carbon monoxide emissions, higher cetane numbers, less smoke and particulates, provide engine lubricity to low sulfur diesel fuels and are biodegradable and non-toxic. In contrast, these fuels can present technical challenges such as: incomplete combustion, elevated NOx emissions, cloud points and cold filter plugging temperatures, high pour points, and low volatility [24]. Besides, long-term application of raw vegetable oils in compression–ignition diesel engines can cause increase carbon deposits on the fuel injectors owing to partial combustion of these fuels. This could eventually lead to weakening of engine performance and cause mechanical damage [25]. Though, this problem could be overcome by notably employing transesterification reaction, a process known to provide high-quality biodiesel fuel [26–28]. In addition, the levels of corrosive sulfuric acid accumulating in engine crank case oil could be lessening because of lack of sulfur in biodiesel fuel [29]. Therefore biodiesel industrialization is much favored. However the economic aspect of its production is the main hurdle. This is mainly due to high cost of feedstocks and low price of fossil fuels [2]. As a result evaluation of economic viability of biodiesel production is the most critical issue, due to high price of virgin vegetable oils [30,31]. The cost of feedstocks is revealed to account for 60–75% of the total cost of biodiesel fuel production [22]. Therefore feedstocks of reduced prices such as waste/used cooking oils are essential to attain commercially viable biodiesel for the future. Waste cooking oil (WCO) possesses much higher acid value than refined vegetable oil due to presence of huge amount of FFAs [32]. For instance, animal fats naturally contain 5–30% FFAs and used cooking oils (UCO) contain 2–7% FFAs and respectively [33]. Recently availability of huge quantities of low-cost fats and oils such as animal fats and restaurant waste oils are reported [22]. The cost of waste cooking oil is 2–3 times low than virgin vegetable oils [34]. Therefore employing less expensive high FFAs feedstocks such as animal fats, waste oils, yellow grease, and brown is expected to appreciably reduce biodiesel cost [35–39]. It has been reported that nearly 55% of United State biodiesel industries use high FFAs feedstocks in producing biodiesel [40]. Another study showed renewable fuel from micro-algal oil to be the only fuel that has the prospect to replace petroleum-derived transport fuels devoid of negatively affecting supply of food and other vital products derived from crops [38].

As earlier stated biodiesel production is expected to benefit from use of low quality feedstocks, but presence of high FFAs in the feedstocks renders it's processing exceedingly difficult. During transesterification, these kinds of feedstocks easily undergo saponification reaction leading to soaps formation. This result in reduced biodiesel yields, especially when alkaline catalyst is used [41]. Figs. 1 and 2 show processes of saponification from FFAs and alkyl esters. Soap formation leads to catalyst consumption, lowering of catalytic efficiency and increase in the viscosity of the biodiesel mixture. It also leads to formation of gels, thus rendering purification of crude biodiesel complicated. However, these problems are reported to be considerably minimized through the application of heterogeneous catalyst such as solids and enzymes catalysts. As well, advances in the production technology could also improve the economics of biodiesel production [42]. Thus, this paper focuses on the production of biodiesel using high free fatty acid feedstocks.

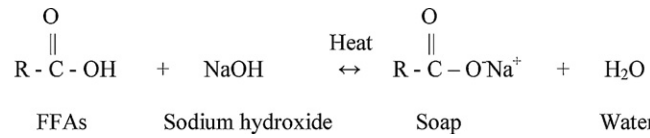


Fig. 1. Saponification from FFAs.

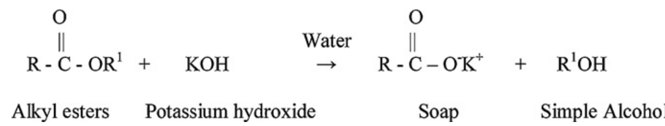


Fig. 2. Saponification from alkyl esters.

Table 1
United State production of fats and oils (billion pounds) [34].

Vegetable oil		Animal fat	
Soybean	18.340	Edible tallow	1.625
Corn	2.420	Inedible tallow	3.859
Peanuts	0.220	Lard and grease	1.306
Sunflower	1.000	Yellow grease	2.633
Cottonseed	1.010	Poultry fat	2.215
Others	0.669		
Total	23.659		11.638

2. High FFAs feedstocks for biodiesel production

The technology to be employed for biodiesel production is usually dependent on the FFAs content of the vegetable oils [43]. Thus the main differences between feedstocks are water content, free fatty acid level and saturation level [44,45].

2.1. Animal fats, grease and waste oils

These categories of feedstocks have already been employed for the production of biodiesel fuel. As earlier stated application of these feedstocks in biodiesel production could lower the cost of final biodiesel product. Canakci [34] have discussed the prospects of restaurant waste oils as feedstock for biodiesel production. The author reported that yearly collection of restaurant waste fats from fast-food establishments and restaurants is approximately 2.5 billion pounds in the United States. Table 1 presents production of fats and oils in the United States. The author noted that cost of yellow grease varies broadly from \$0.09 to \$0.20/lb, with brown grease discounted \$0.01–\$0.03 shown in Table 2 [34]. Another study conducted by Takahashi [46] revealed that the city of Kyoto has used waste cooking oils collected from various sources such as cafeterias, restaurants and households to produce biodiesel fuel to fuel their buses. However, the main hurdles, particularly for waste stream feedstocks such as grease and waste cooking oils are the collection logistics and infrastructure. For instance the collection process

Table 2
The prices of rendering plant products [34].

Bulk	Price range (per pound)	Average price
Animal/livestock feed	\$0.09–0.14	\$0.12
Tallow	\$0.10–0.20	\$0.17
Grease	\$0.07–0.20	\$0.16
Blood	\$0.20	\$0.20
Hydrolyzed feather meal	\$0.125	\$0.125

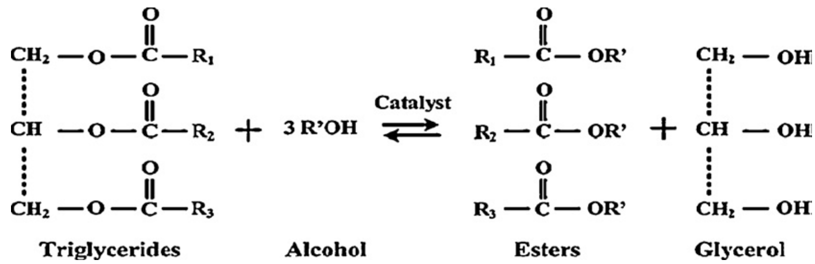


Fig. 3. Transesterification of triglycerides (overall reaction).

might be cumbersome since the sources are usually scattered and lacking any quality control [35].

Further, animal fats, though frequently mentioned, but have not been thoroughly investigated, as compared to vegetable oils because of natural property differences. Among these property differences include solidity at room temperature due to its higher level of saturated fatty acids [47]. Animal fats are more readily available in large quantities in slaughter industries. In these industries the control for the product and handling procedure are usually properly managed. However, there are great concerns relating to biosafety when fats from contaminated animals are used. Thus scientific effort needs to be made to unveil the safety of employing waste animal fats for biodiesel production [35].

2.2. Non-edible oils

The main feedstock sources for biodiesel production from non-edible oils include among others: karanja (*Pongamia pinnata*), Babassue Tree, Canola (Rapeseed), mahua (*Madhuca indica*), Camelina, Honge, Cumaru, Castor, jatropha (*J. curcas*), polanga (*Calophyllum inophyllum*), rubber (*Ficus elastica*), tobacco (*Nicotiana tabacum*), etc. Fatty acid profiles of *P. pinnata*, *C. inophyllum*, *A. indica*, and *J. curcas*, were discovered most appropriate for application as biodiesel. During World War II the seed oil of Jatropha was employed as a petro-diesel fuel alternative and as well blended with diesel. Thus production of renewable fuel as biodiesel is most suitable with *J. curcas* and *P. pinnata* (Karanja). Also, Karanja and Jatropha have high oil content (25–30%) [48]. Also in an attempt to lower biodiesel cost, micro-algal oils have also being experimented by several researchers as raw material for biodiesel production. Compared to energy crops, micro-algae possess higher photosynthetic efficiency, higher biomass production and faster growth [49]. Micro-algal oil contains monounsaturated and saturated fatty acids. The high percentage of monounsaturated and saturated fatty acids in micro-algal oil is considered optimal from a fuel quality standpoint. This property could substantially reduce fuel polymerization during combustion that easily occurs with polyunsaturated fatty-acid-derived fuel [48]. Some of the micro-algal oil sources been investigated for the production of biodiesel includes: *Pseudochoricystis*, *Phaeodactylum*, *Thalassiosira ellipsoidea chlorella*, *Dunaliella tertiolecta*, *Volvox*, *Botryococcus braunii*, *Chlamydomonas*, *Pseudochlorococcum, Chlorella*, and *Dunaliella* [50].

3. Biodiesel production via transesterifiction

3.1. Chemistry of transesterification

Different methods of producing biodiesel from various feedstocks have been developed. These methods are classified as follows: direct oil use/blends with diesel fuel, pyrolysis, microemulsion, and transesterification. The most often used technique to produce biodiesel is the transesterification reaction of vegetable oils with short-chain alcohols, usually methanol [51]. Fig. 3 presents schematic diagram of transesterification reaction of vegetable oil to biodiesel in the presence of catalyst [52]. While, Fig. 4 shows the effects of different production technologies on the yield of methyl esters from various triglycerides containing varying FFAs contents [53].

3.2. Catalytic and non-catalytic transesterification for biodiesel production using high FFAs feedstocks

The immiscibility of fats/oils with alcohols has led to the low conversion of triglycerides to biodiesel products. Therefore, to enhance the reaction rates and achieve better yields, catalysts are mostly employed. Conventionally, homogeneous catalysts such as alkaline catalysts (NaOH, KOH, CH_3ONa, CH_3OK, etc.) and acid catalysts (sulfuric acid, hydrochloric acid, phosphoric acid, etc.) are predominantly used in producing biodiesel. For commercial biodiesel production, alkaline catalysts are the most notably used. Alkaline catalyst such as CH_3ONa is most active, and even if they are applied at low molar concentrations (0.5 mol%) under short reaction times (30 min), biodiesel yield of more 98% can be obtained. However metal alkoxides (CH_3ONa and CH_3OK) are more expensive than alkaline metal hydroxides (NaOH and KOH). Thus the low prices of KOH and NaOH makes them good substitute as they can as well give the same high conversions of vegetable oils, simply by increasing the concentration of the catalyst to 1 or 2 mol% [54]. Other catalysts that are currently being explored in producing biodiesel are heterogeneous catalysts such as solid and enzymes. Heterogeneous catalysts present more benefits for its simpler product separation and purification, catalyst reusability, easier glycerol separation, less energy consumption, etc. Table 3 presents the effects of FFAs content on biodiesel yield.

3.2.1. Homogeneous alkaline and acid catalysts

Alkaline catalysts cannot directly catalyze the transesterification of oils containing high FFAs. It has been reported that

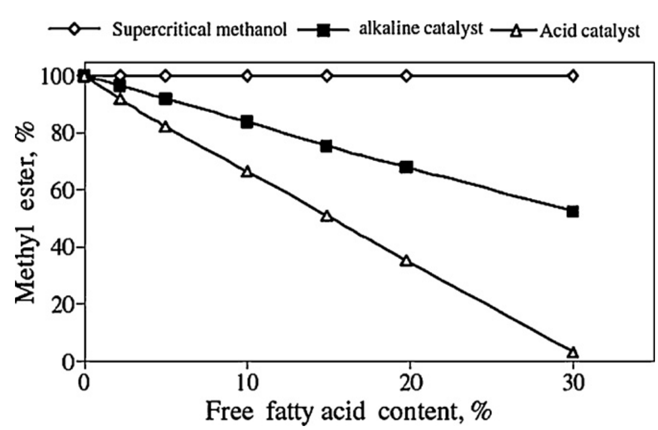


Fig. 4. Yields of methyl esters as a function of FFAs content in the transesterification of triglycerides.

Table 3
The effects of FFAs content on biodiesel yield.

Feedstocks	FFAs content	Catalyst type	Yields	Reference
Waste frying oils	0.42	NaOH	98	[15]
Palm fatty acid distillate (PFAD)	93	H_2SO_4/NaoH	99.7	[37]
Mahua oil	19	H_2SO_4/KOH	98	[55]
Calophyllum inophyllum	22/<2	H_2SO_4/KOH	85	[56]
Jatropha curcas oil	28	H_2SO_4/KOH	90–95	[57]
Tobacco seed oil	<2.0	H_2SO_4/NaOH	91	[58]
Waste cooking oil	2.56	CaO	99	[59]
Acid oil	59.3	H_2SO_4	95	[60]
Tall oil	100	HCl	–	[61]
Jatropha curcas	14/<1	H_2SO_4/KOH	99	[62].
Brown grease	40/<1	Diarylammonium catalysts $NaOCH_3$	98	[63]
Waste fryer grease	5.6	H_2SO_4/KOH	90	[64].
Heterotrophic microalgal	8.97	H_2SO_4		[65]
Sunflower oil	–	CaO/SBA-14	95	[66]
Sorghum bug oil	10.5	H_2SO_4	77.4/97.6	[67]
Madhuca indica	20	Pseudomonas cepacia	96	[68]
Fat from meat and bone meal	11	H_2SO_4/KOH	45.7	[69]
Canola Oil	0.04	NaOH	98	[70]
Micro-algal oil	20–50 [50]	Con H_2SO_4	58	[65]

for alkaline transesterification to take place, the FFAs level in the oil should be below a desired level (ranging from less than 0.5% to less than 3%) [71]. As a result a two-step transesterification is usually employed to prepare biodiesel from high FFAs feedstocks. In this technique, the raw material undergoes acid pretreatment before being subjected to alkali-catalyzed transestrification. Acid-catalyzed chemical reaction also referred to as esterification involving reaction of FFAs and alcohol yielding fatty acid alkyl ester and water. It has been remarked that acid catalysis is more tolerant to high FFAs and moisture levels in the initial feedstocks and therefore, more appropriate for low-quality greases and fats [36,47]. Further, Canakci [34] stated the need to reduce the FFAs in oil by using an acidic-catalyzed technique, because of the difficulties involved in processing low quality feedstocks via alkaline catalysts. In the same way, Ghadge and Raheman [55] stated that conversion of feedstocks to biodiesel via alkaline catalyst is difficult with oil having huge quantities of FFAs (41%w/w). Thus the high FFAs mahua oil (19%) was pretreated using different reaction times of 0.5, 1.0, 1.5, 2.0 h and methanol to oil molar ratios of 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40. The final product containing acid value less than 2 mg KOH/g using lowest reaction time and methanol amount in the second step was employed for the main transesterification reaction. The transesterification reaction was conducted with 0.7% w/v KOH as an alkaline catalyst and 0.25 v/v methanol (6:1 molar ratio). The KOH amount was determined based on the amount required to neutralize the unreacted acids (i.e. 2 mg KOH/g) in the second step product plus 0.5% for catalyst. The reaction was conducted for half an hour at 60 °C. Consequently mahua biodiesel yield of 98 wt% was obtained. Also the fuel properties of mahua biodiesel met both European and American standard specifications for biodiesel. Fig. 5 presents conventional schematic diagram for producing biodiesel fuel. In another study, Usta et al. [72] reported that soapstock contains large amounts of FFAs ranging from 45 to 50%. And that oil containing high FFAs cannot be effectively transformed to biodiesel fuel using only an alkaline catalyst. The high FFAs feedstock was esterified using acid (H_2SO_4) catalyst and then transesterified via base (NaOH) catalyst to produce biodiesel. They noted some reduction in viscosity of the mixture via the process, at low temperatures, the viscosity of the biodiesel produced was higher compared to those provided by petro-diesel fuel.

Furthermore, palm fatty acid distillate (PFAD) a by-product from palm oil, with FFAs content of 93 wt% as feedstock was used in producing biodiesel. The esterification and purification processes yielded high-quality biodiesel with a clear brown color and most of the fuel properties met the American biodiesel standard specification [37]. Similarly, Wang et al. [73] adopted a two step catalyzed process and prepared biodiesel from waste cooking oil whose acid value was 75.92 ± 0.036 mg KOH/g and got final product of 97.02 wt% of biodiesel. Fig. 6 depicts esterification reaction of FFAs to alkyl esters [40]. Also, Zullaikah et al. [74] employed a

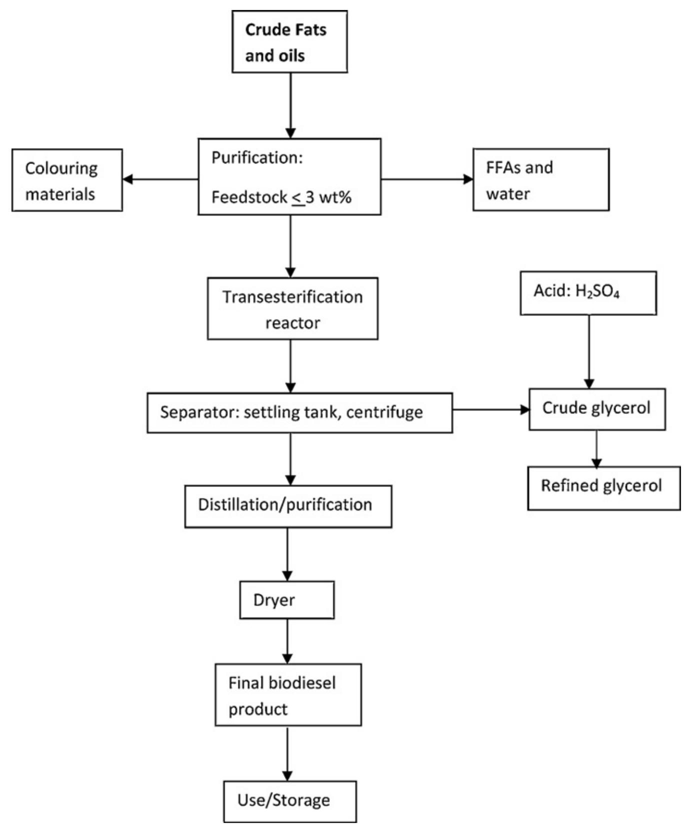


Fig. 5. Conventional schematic diagram for the production of biodiesel fuel.

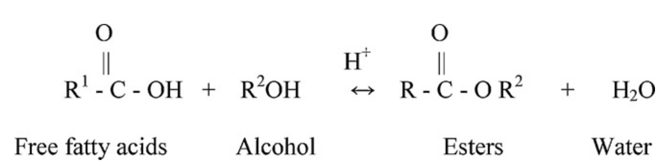


Fig. 6. Esterifcation reaction.

two-step acid-catalyzed methanolysis process to convert more than 98% FFAs and less than 35% of triglycerides (TG) of rice bran oil in 8 h. On the other hand, Van Gerpen et al. [75] remarked that an alternative route to use high FFAs raw materials is to employ a base catalyst to deliberately form soap from the FFAs. The soap formed is recovered, the oil dried, and then use in a conventional base catalyzed system [75].

Miao and Wu [65] have produced biodiesel from micro-alga *C. protothecoides* using 100% H_2SO_4 based on oil weight), six levels of molar ratio of methanol to oil (25:1, 30:1, 45:1, 56:1, 70:1 and 84:1) and three different temperatures (30, 50 and 90 °C). At optimum conditions (temperature of 30 °C and 56:1 molar ratio of methanol to oil), the product specific gravity was reduced from an initial value of 0.912 to a final value of 0.8637 in about 4 h of reaction time.

3.2.2. Heterogeneous catalysts

These catalysts are either solid or enzymes and have shown great efficiencies in producing biodiesel fuels. Thus, solid and enzymes catalysts have being increasingly reported to show great promise for producing biodiesel using low quality feedstocks. Heterogeneous catalyst is reportedly used in biodiesel plant of Diester Industrie (Paris) at Sete, France. The Esterfip-H process produces biodiesel (fatty acid methyl esters (FAME)) by esterification of plant oils such as sunflower, soybean and rapeseed. This catalyst eradicates a number of refining steps required for processes conducted via homogeneous catalysts. Besides the purity of biodiesel exceeds 99%, with nearly 100% biodiesel yield. In addition, biodiesel production via heterogeneous catalyst route generates by-product, glycerol with purity higher than 98% compared to homogeneous process which provide glycerol purity of about 80%. Thus the utilization of by-product, glycerol could improve the overall production economic [54].

3.2.2.1. Solid catalysts. Solid super acids such as Sulfated zirconia and tungstated zirconi can significantly promote the transesterification of vegetable oils as well as the esterification of FFAs [76]. Gupta [43] reported that solid catalysts tolerates feedstocks with higher levels of FFAs and needs no pretreatment or removal of FFAs. The author noted the conversion of FFAs present in feed oils to biodiesel. Also, Suppes et al. [77] have transesterified soybean oil containing roughly 2.6 wt% FFAs with methanol at 60, 120, and 150 °C in the presence of a series of catalysts such as ETS-10 zeolite NaX faujasite zeolite, and metal catalysts. The experiments were carried out using 6:1 alcohol to oil molar ratio. The authors noted that a preliminary design evaluation showed that the catalysts are sufficiently active to be industrially viable. Besides, conversions in excess of 90% at a temperature below 125 °C are easily achievable. In another study, Banerjee and Chakraborty [32] reported esterification of FFAs present in waste cooking oil via heterogeneous acid catalysts such as WO_3/ZrO_2. The authors noted that the catalyst is more efficient compared to homogeneous acid catalysts, owing to their simplicity of product separation and prevention of pollution. Similarly, Kim et al. [78] employed Na/NaOH/γ-Al_2O_3 base catalyst to convert soybean oil to biodiesel. The authors employed a 100 ml stainless steel batch reactor equipped with a cooling jacket and a stirrer surrounded by a heating mantle controlled by a proportional integral derivative (PID) temperature controller to carry out the transesterification process. The reactor was fed with 18.3 ml of methanol (molar ratio of methanol to soy bean oil 9:1), fifty milliliters of soy bean oil, 10 ml of *n*-hexane and 1 g of catalyst, and the temperature was raised to 60 °C under stirring at 300 rpm for 2 h. They noted that under optimized reaction conditions, the activity of Na/NaOH/γ-Al_2O_3 base catalyst was almost comparable to NaOH catalyst. Another study conducted by Janaun and Ellis [35] revealed that transesterification via sulfated zirconia–alumina (SZA), amberlyst-15 (sulfonated polystyrene-based resin), nafion NR50 (perfluorinated alkane sulfonic acid resin), tungstated zirconia–alumina (WZA), and sulfated tin oxide (STO), and solid base catalysts such as oxides, alkoxides and alkaline-earth metal hydroxide such as CaO, $Ca(CH_3O)_2$ and $Ca(OH)_2$ and metal compounds such as Al_2O_3/ZrO_2, ZnO, TiO_2/ZrO_2 and ferric sulfate are widely studied. The authors noted that since transesterification reaction catalyzed by solid acid catalysts is less affected by the presence of FFAs and water, therefore solid acid catalysts have an advantage over solid base catalysts. In additionally, the ability of solid acid catalysts to carry out transesterification of triglycerides and esterification of FFAs simultaneously placed them at an advantage compared to other base solid catalysts. Therefore, a solid acid catalyst is most suitable for low-grade feedstocks. Thus the process is envisaged to lower the overall biodiesel production costs. Kouzu et al. [59] transesterified WCO containing acid value (5.1 mg KOH/g) using CaO catalyst. The yield of FAME was above 99 wt% at 2 h. Further, Taufiq-Yap et al. [79] have used calcium-based mixed oxides catalysts (CaZnO and CaMgO) to transesterify *Jatropha curcas* oil (JCO) with short-chain methanol, so as to evaluate their potential as heterogeneous catalysts for the production of biodiesel. Thus their conversions were compared with zinc oxide (ZnO), magnesium oxide (MgO) and calcium oxide (CaO) catalysts. The transesterification reactions were conducted at: reaction temperature, 338 K, reaction time, 6 h%; methanol/oil ratio, 15:1 and catalyst amount, 4 wt. Among the experimented catalysts, MgO catalyst showed very low conversion of JCO (∼10%), whereas no biodiesel was produced when non-active ZnO was used. The use of CaO provided highest catalytic activity with JCO conversion of 85%. Amusingly, the conversion of JCO to biodiesel using calcium based mixed metal oxides (CaMgO and CaZnO) presented biodiesel yields of 83% and 81%, respectively. The higher conversion of CaO catalyst in shorter time compared to CaMgO and CaZnO, was attributed to the slightly solubility of CaO catalyst in the liquid reaction. The conversion of JCO via CaO was significantly affected after the forth run while the conversion was only slightly lowered for CaMgO and CaZnO after sixth run.

Also, Shi et al. [80] conducted an experimental study on preparation and characterization of the organic–inorganic hybrid membrane to produce biodiesel. The authors revealed that esterification results show the FFAs conversions to esters were 94.5% for $Zr(SO_4)_2$/SPVA catalytic membrane and 81.2% for $Zr(SO_4)_2$/PVA catalytic membrane. Schultz et al. [81] developed amberlyst BD20, a heterogeneous catalyst, for a continuous process to convert FFAs in low-cost feedstocks to biodiesel fuel. In another study, Dalai et al. [82] compared performance of heterogeneous catalyst (zeolite, CaO, MgO, Li/CaO, $Ba(OH)_2$) and homogeneous catalyst (KOH) in transesterifying vegetable oil to biodiesel fuel. The authors remarked that among all the heterogeneous catalysts investigated, $Ba(OH)_2$ catalyst provided better performance yielding 99 wt% esters in 480 min. They noted the performance of the catalyst to be comparable to that of KOH. Jacobson et al. [83] evaluated various solid acid catalysts to produce biodiesel from high FFAs oil such as waste cooking oil containing 15 wt% FFAs. They reported that zinc stearate immobilized on silica gel (ZS/Si) was the most efficient catalyst in simultaneously catalyzing the esterification of FFAs present in WCO and transesterification of oils to biodiesel. Hence the process presented maximum biodiesel yield of 98 wt%. Karmee and Chadha [84] have transesterified non-edible oil, *P. pinnata* using solid acid catalysts such as Montmorillonite K-10, ZnO and Hb-zeolite. A conversion of 83% for ZnO and low conversion of 47–59% for Hb-zeolite and Montmorillonite K-10 were recorded.

Further, Preiss and Kowalski [50] have reported the ‘Mcgyan’ method, in which micro-algal oil is transformed to fatty acid alkyl esters (FAAE) using both supercritical and catalysis conditions. The method is a major innovation toward cost-effective and more efficient production of FAAE from micro-algal oil. The method enables

Table 4
Preferential order of catalyst selection for the production of biodiesel from high to low quality feedstocks.

FFAs (wt%)	Preferential order	Catalyst characteristic	Catalyst separation	Cost of catalyst	Reaction conditions
<3	Alkaline catalyst	High catalytic efficiency, higher conversion/yield (>98), less corrosive on industrial equipment	Difficult	Cheap	Moderate temperature, of alcohol to oil (6:1) pressure, molar ratio and short reaction time
>3	Acid/alkaline catalyst	Highly efficient, better yield (98%) and superior quality biodiesel than acid catalyst	Difficult	Reasonable cost	Moderate reaction conditions
>3	Solid acid catalyst	Lower catalytic efficiency compared to solid alkaline catalyst, but higher stability. Catalyzes both esterification of FFAs and transesterification of triglycerides simultaneously. Further used in many industrial processes.	Easily separated from biodiesel	High catalyst cost	Moderate/high reaction conditions
>3	Solid alkaline catalyst	Higher catalytic activity than solid acid catalyst, but easily deactivated	Easily removed from biodiesel product	High cost of catalyst	Moderate/high reaction conditions
>3	Enzymes	They catalytically efficient, highly selective, involves less energy consumption. But easily inactivated by methanol. Also easily deactivated by glycerol. They as well require minimum water content to function effectively. They are also easily leached.	Easily separated	High catalyst cost	Mild conditions of reaction
>3	Acid catalyst	Low catalytic activity, sensitive to water concentration, but less, susceptible to presence of FFAs, catalyst deactivation by hydration	Cumbersome	Moderate cost	Higher alcohol to oil molar ratios, low temperature and pressure, high acid catalyst concentrations

The table provides a general guide for the selection of best catalyst to use for the production of biodiesel from high to low quality feedstocks. For refined feedstocks (FFAs < 3%), liquid alkaline catalyst is best. However for low quality feedstocks (FFAs > 3%), the order of catalyst selection is as follows: acid/alkaline catalyst > solid acid catalyst > alkaline catalyst >enzyme catalyst > liquid acid catalyst.

fast, consistent and cost-effective conversion of high FFAs feedstocks, using continuous transesterification of oil by charging oil and alcohol mixtures through a fixed bed reactor using metal–oxide catalysts. The Mcgyan method has been demonstrated to be very promising. By exhibiting a FAAE conversion rate greater than 90% for micro-algal oil with a residence time of about 60 s. Also, the Mcgyan process can be operated industrially using porous alumina, titania and zirconia microspheres with supercritical alcohol for continuous long-term FAAE production (for greater than 115 h) without loss of conversion rate or catalytic activity [50].

3.2.2.2. Enzyme catalysts. Enzymatic-catalyzed transesterification of triglycerides offers more environmentally attractive alternative to the conventional process [85]. The latest data suggests that enzyme catalysts can be useful and cost saving [86]. Balat and Balat [87] noted that transesterification process is usually catalyzed by different lipases such as *Candida*, *Pseudomonas* sp., *Pseudomonas cepacia*, *Candida rugasa*, *Rhizomucor miehei* and immobilized lipase (lipozyme RMIM). The authors noted emphasize made on advantages of lipase-catalyzed transesterification in comparison to chemically catalyzed transesterification reaction. Casimir et al. [88] reported conversion of waste oil containing high FFAs feedstock to biodiesel fuel using lipase catalyst to offer greater than 90% yield. The activities of the lipase remain active for a period of more than three months. Furthermore, the interference of acid and base catalyzed-tranesterification reaction by FFAs and water can be easily overcome by enzymatic methods [89,90]. Ghaly et al. [91] noted that besides choice of lipase to be used. The feasibility of transesterification process and its readiness to industrialization is controlled by certain factors such as: water activity/content and reaction temperature, the selection of feedstock and alcohol, enzyme modification, pretreatment of the lipase, alcohol to oil molar ratio, and use of common solvents. The authors noted the essentiality to decrease the cost of biodiesel production via optimization of these parameters. Modi et al. [92] have employed ethyl acetate in producing biodiesel from crude oils of *Helianthus annus* (sunflower), *P. pinnata* (karanj), *J. curcas* (jatropha) via immobilized Novozym 435-catalyzed interesterification to yield 91.3, 90, and 92.7% biodiesels, respectively. The reaction was carried out at a molar ratio of 11:1 ethyl acetate/oil, a temperature of 50 °C, and reaction time of 12 h. The reaction was repeated severally (12 times) without significant loss in enzyme catalytic activity when ethyl acetate was used as an acyl acceptor, but using ethanol as the acceptor, the activity of the enzyme diminished after six cycles. Additionally, the separation of biodiesels produced from the reaction mixtures were conducted via column chromatography, with a column packed with 30 g of 60–120 mesh silica gels by eluting with 600 mL of hexane/diethyl ether, 99.5:0.5, v/v. In another study, Li et al. [93] combined two microbial lipases (1% Novozym 435, nonspecific and 3% lipozyme TL IM, 1,3-specific) in the reaction. A molar ratio of methanol/oil of 4:1 and a volume ratio of *t*-butanol/oil of 1:1 were employed to carry out the reaction for 12 h at 35 °C, which provided 95% biodiesel yield. The catalytic activity of the lipase was maintained even after 100 days, which represented 200 cycles of utilization. The process is proven to be suitable for both feedstocks having low FFAs content (refined oils; 1.8% FFAs) and high FFAs feedstocks (waste oils; 70% FFAs). The authors reported that achievement of over 90% yield of biodiesel was due to the presence of molecular sieves in the dehydrated waste oil.

Generally, the amount of FFAs content in various feedstocks influences the selection of a catalyst to be used for the production of biodiesel fuel. Table 4 presents general guide of catalyst selection for the production of biodiesel from high to low quality feedstocks.

3.2.3. Supercritical methanol

Voll et al. [18] remarked on the non-catalytic reaction, using alcohol under supercritical conditions at high temperatures and pressures. Thus the features of the supercritical method allows various resources such as swill oil and frying oil to be used as the feedstocks, thus esters yield can be more than 96% [94]. Similarly,

Van Kasteren and Nisworo [95] reported that since waste cooking oil contains FFAs, adopting supercritical transesterification could offer huge advantages by erasing pre-treatment capital and running cost. Also, the presence of FFAs in feedstocks during transesterification with various supercritical alcohols does not have a significant effect on the yield [96]. Demirbas [17] studied transesterification of cottonseed oil to biodiesel in non-catalytic SCF conditions. The authors noted that transesterfication of linseed oil in SCF such as methanol and ethanol has proved to be the most promising process. Supercritical methanol is a high-density chemically labile vapor that cannot be compressed into the liquid state (80 bar, 240 °C). Supercritical methanol is miscible with oils and fats or FFAs [97]. It has been observed that supercritical methanol process for the transesterification of fats and oils can tolerate presence of higher FFAs [35]. Saka and Kusdiana [98] stated the yield of esters produced by supercritical methanol method (SCM) is higher than that of the common method. Thus, the conversion of FFAs to methyl esters in supercritical process led to the increase yield. In common method, FFAs, is converted to saponified products by the alkaline catalyst. The authors recently found that these same FFAs are converted to methyl esters through the dehydration reaction during the supercritical treatment of methanol [98].

Further, Imahara et al. [99] noted that non-catalytic supercritical methanol technologies are attractive processes in biodiesel production by overcoming problems such as incomplete conversion of oils/fats because of presence of FFAs. Also, Banerjee and Chakraborty [32] noted that non-catalystic supercritical transesterification of WCO has provided biodiesel of high purity (99.8%) and almost pure glycerol (96.4%). It has been also reported that, supercritical methanol with a co-solvent process is superior to the conventional supercritical methanol method, thus providing more than 98 wt% yield of methyl esters [100]. Additionally high conversions of 80–100% were recorded when the reaction was conducted in supercritical methanol and ethanol. However, reaction catalyzed by an enzyme in supercritical carbon dioxide provided low conversions of 27–30% [101].

3.3. Properties of biodiesel fuel

The fuel properties of biodiesel are close to petro-diesel fuels. Biodiesel fuels are characterized for their physical and main fuel properties such as flash point, density, higher heating value (HHV) and viscosity [17]. The advantages of biodiesel combustion over petroleum diesel are well established [102,103]. Biodiesel is regarded as a neat fuel because it has no aromatics, no sulphur, and has about 10% built in oxygen, which facilitates it to burn fully and its higher cetane number enhances the ignition quality [47,104]. Dorado et al. [105] reported exhaust emissions profile from a diesel engine fueled with transesterified waste olive oil containing high FFAs. They remarked that use of biodiesel provided lower emissions of CO_2 (up to 8.6%, excepting a case which presented a 7.4% increase), CO (up to 58.9%), NO (up to 37.5%), with increase in emissions of NO_2 (up to 81%, excepting a case which presented a slight reduction) and SO_2 (up to 57.7%). Thus the slight increase in brake-specific fuel consumption (lower than 8.5%) presented by biodiesel fuel may be tolerated due to the exhaust emission benefits. Also the authors noted the combustion efficiency to remain constant. In addition fuel viscosity plays an important role in the combustion of fuel used [106]. Similarly, Lapuerta et al. [107] studied the effect of biodiesel fuels on diesel engine emission. The authors noted that the emission of aromatic and polyaromatic compounds, as well as their toxic and mutagenic effect, has been generally considered to be reduced with biodiesel. Lin et al. [108] noted that biodiesel has low poison, high cetane number and flash point, high biodegradability, high oxygen content and superior lubricity. The authors inferred fuel properties of biodiesel fuel to be improved by peroxidation process. Haas et al. [109] noted that application of soy soapstock biodiesel in diesel engines present similar emissions and performance to those of biodiesel fuel from soy oil. Also, Kaul et al. [110] have determined corrosion characteristics of biodiesel from non-edible oils like *M. indica* (Mahua), *Pongamia glabra* (Karanja), *J. curcas*, and *Salvadora oleoides* (Pilu) of Indian origin on diesel engine parts. The authors stated that corrosion on both metal parts of diesel engine was shown by biodiesel produced from *S. oleoides* (Pilu) while little or/no corrosion as compared to neat diesel shown by biodiesel produced from other oils.

Table 5
The effects of FFAs on the quality of biodiesel fuel.

Impurity	Effects of impurity	Reference
FFAs	A significant number of fuel properties kinematic viscosity, lubricity, low temperature performance, and oxidative stability might be impacted in the presence of FFAs in biodiesel fuel	[114]
	Presence of FFAs could negatively affect biodiesel oxidative stability	[115]
	Occurrence of FFAs in biodiesel fuel could significantly raises its kinematic viscosity	[111,116]
	Corrosion and low oxidation stability	[117]

Further, Knothe and Steidley [111] reported that to improve the low-temperature properties of biodiesel fuel produced from waste cooking oil, winterization, a process consisting of several cooling cycles with resulting filtration to remove higher-melting components from a mixture, was applied. The authors noted that parameters such as peroxide value and acid value increased when biodiesel fuel produced from used frying oils were stored over a long period of time. Leung et al. [112] studied degradation of biodiesel under different storage conditions. The results suggested increase in biodiesel degradation rate at high temperature, with air exposure. Biodiesel degradation is little affected by temperature or air exposure alone. Phan and Phan [38] stated that carbon residue was much higher in the biodiesel than in diesel inspite of the fact that most of the physical properties of the biodiesel were within standards for diesel fuel and for bio-auto fuels (EN14214). The carbon residue was only 0.05 wt% for diesel but 4.0 wt% for the biodiesel. Additionally, distillation curve clearly projected volatility characteristics of the biodiesel to be much different to that of diesel fuel. Also, Pugazhvadivu et al. [113] noted that, with the increase in FFAs content of oil, the oil becomes viscous, leading decrease in calorific value of the fuel.

Felizardo et al. [15] reported that presence of FFAs influences fuel aging; the European Standards specifies a maximum value of 0.5 mg of KOH/g of sample. Table 5 presents the effects of FFAs on the quality of biodiesel fuel.

3.4. Biodiesel economic evaluation

Biodiesel provides several advantages such as decrease in greenhouse gas emissions, improves the lubricating property [118], and helps in reducing country's over-reliance on the importation of crude oil imports. It also supports agriculture activities by providing a new labor and market opportunities for domestic crops. And it is broadly accepted by vehicle manufacturers [119]. The statistic of world biodiesel production revealed, 42% of the global total in 2006 was accounted for by Germany, where market conditions were favorable as shown Fig. 7. Other countries with major biodiesel markets in 2006 included United States, France, Italy, and the United Kingdom [87]. Another biodiesel industrial economic benefit would include: increment in income taxes, increase number of manufacturing jobs in rural and remote areas, investments in plant and equipment and feedstocks added value. Present

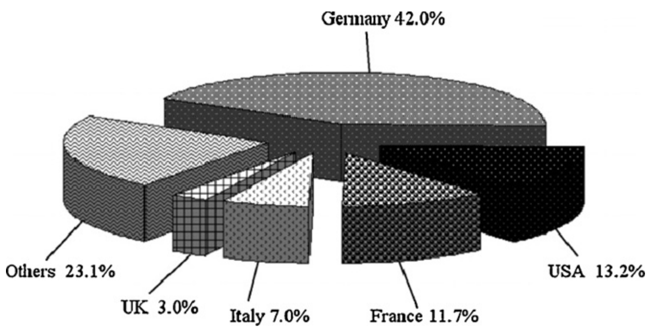


Fig. 7. The top five biodiesel producers in 2006.

increase in biodiesel potential is not only in the number of plants, but also in the size of the production facilities. The remarkable development in biodiesel industrial activities is anticipated to have momentous effects on the cost of feedstocks used for biodiesel production [9]. Currently, soybean oil, alkaline catalyst and short-chain alcohol, methanol are used to produce biodiesel, however the huge quantities of less cost fats and oils such as animal fats and restaurant wastes that could be converted to biodiesel have lessen the problems faced in using soybean oil as feedstock for biodiesel production. Furthermore the costs of biodiesel from oilseed or animal fats have been projected by economic feasibility. The costs ranged from US$0.30 to 0.69/l, including meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Biodiesel cost from waste grease and vegetable oil are, roughly projected to be US$0.34–0.42/l and US$0.54–0.62/l respectively. Presently biodiesel, is not economically realistic, therefore more development in research and technology will be needed because of pre-tax diesel is priced at US$0.20–0.24/l in some European countries and US$0.18/l in the United States [119]. However, Preiss and Kowalski [50] noted that if less expensive feedstocks are used to produce biodiesel, a 25% reduction in cost production is possible (all other production costs kept equal). Also, Bender [120] stated that approximate projections of the cost of biodiesel fuel produced from vegetable oil and waste grease areUS$0.54 $\pm$ 0.62/l and US$0.34 $\pm$ 0.42/l, respectively. Chisti [42] reported that biodiesel from palm oil costs around $0.66/l or 35% higher than petroleum diesel. This suggests converting palm oil to biodiesel fuel adds about $0.14/l to the price of oil. Also for biodiesel from palm oil to be competitive with petrodiesel, the price of palm oil should not go beyond $0.48/l, assuming absence of tax on biodiesel. By means of similar equivalence, a considerable target price for micro algal oil is $0.48/l for algal-derived diesel fuel to be cost competitive with petroleum diesel [121]. Demirbas [38] stated that soon, algae will become the most important biofuel source. The author further stated that microalgae appear to be the only source of renewable biodiesel that can meet the global demand for transport fuels.

West et al. [122] and Zhang et al. [123] employed HYSYS simulator to carry out economic comparison between different biodiesel production techniques. The reports reveal that biodiesel produced via heterogeneous catalyzed process presents lowest total capital and production cost and is positive after rate-of-return for a plant capacity of 8000 mt/yr. Also, Hass et al. [109] carried out economic analysis to produce biodiesel by using low value triglycerides as feedstocks. It has been suggested that vegetable oil soapstock used in producing biodiesel would be nearly cost US$ 0.41/l, a 25% reduction relative to the estimated cost of biodiesel produced from soy oil [124]. Biodiesel production cost was reported to vary inversely and linearly with variations in the market value of glycerol, increasing by US$0.0022/l ($0.0085/gal) for every US$0.022/kg ($0.01/lb) decrease in glycerol value. The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost. So also the changes in process chemistry and technology, the changes in the type of feedstock employed, and changes in the value of the glycerol co-product [109]. Carraretto et al. [125] noted that biodiesel cost is dependent on the places where the soy beans are grown and the type of agriculture technologies used. The authors noted the diesel fuel in Italy is about 2–3 times lower than the average cost of biodiesel, without considering tax and VAT. They further revealed that the running cost with biodiesel and diesel oil would be similar (+0.64% for biodiesel) if the efficiency improvement is disregarded. They highlighted that the different density, economic cost of the fuel and the engine performance are the main items influencing the running cost. Szulczyk and McCar [126] noted that a simulation model can help to predict biodiesel market penetration given various fossil fuel prices. The authors stated that higher fossil fuel prices raises an agricultural producer's cultivation, harvesting, and processing costs, but also boost prices for biodiesel.

4. Challenges and prospects of high FFAs feedstocks for the production of biodiesel

4.1. Challenges of high FFAs feedstocks in producing biodiesel fuel

The production of biodiesel fuel from oil crops is significantly increasing as a clean-burning alternative fuel, but its production in huge amount is not sustainable [127]. Khan [128] remarked that because of the conflict with food supply, viability of the first generation biofuels production is really questionable. On the other hand, the major problem associated with processing low-cost fats and oils is that they have high quantities of FFAs that cannot be easily transformed to biodiesel fuel by conventional alkali-catalyzed transesterification [129,130]. This is because FFAs are a potential contaminant in oils and fats [44]. Singh and Singh [47] reported that waste greases naturally have FFAs ranging 10–25%. Thus such amount is far above the level that can be transformed to biodiesel fuel using an alkaline catalyst. Therefore during transesterification, fats and oils containing high FFAs value need more NaOH to neutralize the FFAs [131]. Kusdiana and Saka [132] remarked that, in the conventional transesterification of oils and fats to produce biodiesel fuel, FFAs always create negative effects. This is because presence of FFAs produces soaps formation, thus reducing catalytic performance, all of which bring about low conversion. Several researchers have found out that FFAs and moisture contents in oils were major factors affecting alkali-catalyzed transesterification. Another reports suggested that the FFAs content in the oil should be less than 1 wt% before alkali-catalyzed transesterification [133]. Also, production of biodiesel via acid-catalyzed conversion of low-cost feedstocks forms large amount of water, which negatively affect biodiesel production since water can hydrolyze the ester products and produce FFAs [36]. Similarly, Hass [134] remarked the most difficult factor with soapstock (SS), contrary to virgin fats and oils and recycled greases is that, it contains large quantity of water. Therefore ransesterification reaction is rendered difficult, since water competes with the alcohol, converting the preferred alkyl ester transfer reaction into ester hydrolysis and producing FFAs. Van Gerpen et al. [75] reported that direct acid esterification of high FFAs feedstocks needs removal of water during the reaction, or the reaction will be prematurely quenched. Further, Demirbas [7] noted that the yield of biodiesel plummets to 6% with an increase in FFAs content to 5.3 wt%. In another study, Boz et al. [135] reported that, since conversion efficiencies of biodiesel depends on FFAs and water content, the existing industrial facilities for biodiesel production process made provision only for the use of high-purity and quality virgin oils with negligible FFAs concentrations.

Table 6
Fatty acid composition of some low quality feedstocks.

Fatty acids	Content (wt%)							
	Mahua oil [55]	Jatropha oil [56]	Tallow [137]	Scum oil [138]	Micro-algal oil [127]	*Balanites aegyptiaca* [114]	*Z. bungeanum* [139]	*Terminalia catappa* [70]
Myristic acid		–	2.8	14.3526				
Palmitic acid	16.0–28.2	15.6	23.3	42.1390	12–1	13.713.7	10.6	35.0
Palmitoleic acid		–			55–7		5.2	
Stearic acid	20.0–25.1	6.5	19.4	15.7632	1–2	11.1	1.4	5.0
Oleic acid	41.0–51.0	43.5	42.4	19.2093	58–60	43.7	32.1	32.0
Linoleic acid	8.9–13.7	34.4	2.9	0.4822	4–20	31.5	25.6	28.0
Linolenic acid	0.80		0.9	0.2509	14–30	24.1		
Arachidic acid	0.0–3.3	–						
Lauric			0.1	2.7176				

Contrary to the use of homogeneous catalyst, Leung et al. [136] stated that, solid catalysts are suitable in the transesterification of high FFAs feedstocks, but the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction. Also, Casimir et al. [88] remarked that crude and waste oils and used frying oils from the refinery contain impurities such as phospholipids, water and FFAs during the transesterification reaction may inactivate lipase catalyst. In another study, Wang et al. [96] reported that, although transesterification by supercritical alcohols can tolerate presence of high FFAs in feedstocks. But it reaction requires pressures of 45–65 MPa and temperature of 350–400 °C, which is not a practical in the industry.

4.2. Prospects of high FFAs feedstocks for biodiesel production

The use of low cost feedstocks to produce biodiesel fuel is envisaged to provide economically viable biodiesel that can favorably compete with petro-diesel [34]. Additionally, Ghaly et al. [91] remarked that use of low price waste materials as feedstocks to produce biodiesel fuel will have double environmental benefits by producing an environmentally friendly fuel and decreasing the environmental pollution potential of the wastes. Some of the feedstocks containing high amount of FFAs include among others; lard, soapstock, mahua oil, jatropha oil, tallow, and vegetable oils from restaurants and household disposals. These feedstocks comprises of varieties of fatty acid compositions as shown in Table 6. Using waste cooking oils as feedstocks, the feasibility of a continuous transesterification process and recovery of glycerol of high-quality as by-product are prime alternatives to be considered to reduce the cost of biodiesel fuel [119]. Similarly, methanolysis of used frying oils to produce biodiesel fuel is another possibility to produce less costly alternative fuels, which could decrease pollution and protect the environment [140]. Achten et al. [141] reviewed the potentials of jatropha biodiesel production and its use. The authors noted that the impact on the soil and environment seems to be positive. Even though, the cost of jatropha is not yet clearly determined. Biswas et al. [142] reported that a simplified process for biodiesel production was developed by CSMCRI from the oil complying with Euro-3 specifications for free fatty acid methyl ester. Another important step in the development of biodiesel is the discovery of micro-algal oil as feedstocks. Microalgae biomass appears to be another viable alternative for producing economically viable biodiesel products. The oil productivity of many microalgae surpassed the best producing oil crops. Also, oil content in microalgae can exceed 80% by weight of dry biomass [128]. Additionally, tremendous successes have been recorded in changing composition of oleaginous microorganisms to make them suitable in the actual biodiesel production, and modifying the fatty acid by genetic engineering methods. Thus, synthesis of lipids with varying fatty acid composition should be feasible by culturing oleaginous microorganism under different conditions, and by metabolic regulation. In 1990s, temperature-induced changes are reported in the fatty acid composition of the accumulated lipids of various oleaginous microbial cells [143].

5. Conclusions and recommendations

Based on the research conducted, the following conclusions and recommendations were made:

a. It was found that, high cost of refined feedstocks has made biodiesel production less economical and uncompetitive with conventional diesel fuel.
b. Biodiesel produced from low quality feedstocks were reported to benefit from lower prices of the feedstocks and are largely available.
c. The physicochemical properties of biodiesel from low quality feedstocks were observed to be similar to that of diesel fuel, therefore a major boost in the technology of biodiesel production.
d. A more efficient and effective technology needs to be developed to perfectly process high FFAs feedstocks to harness its potentials to the fullest.
e. Pronounced emphasis also need to be made on non-edible feedstocks such as *J. curcas*, pongamia, and castor oil beside waste cooking oils, soapstock and animal fats for producing biodiesel.
f. Mass campaigns by global organization and policy makers to encourage the populace to engage in the realization of renewable energy such as biodiesel to make the society safer for a living and continue existence is needed.

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